# θ -> α Phase Transition in Thermally Grown Aluminas: Mechanisms and Control

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#### Motivation

- Structural components operating at high temperatures (e.g., turbine blades) rely on thermally grown oxides for corrosion protection.
- · For longer lifetime operation and higher operating temperatures, improved oxides are needed.
- · For this purpose, improved understanding of oxide growth mechanisms is needed.

#### Introduction

- The first formed oxide is  $\theta$ -Al<sub>2</sub>O<sub>3</sub> which transforms to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at T>1000C.
- But corrosion protection is provided by α-Al<sub>2</sub>O<sub>3</sub>.
- The probability of failure increases with oxide thickness.
- Thus, it is desirable to accelerate the transformation to keep oxide thin.

### Accomplishment

- We establish that the early stage  $\theta$ -phase development is strongly influenced by the presence of external nucleation sites and that these sites can be exploited to dramatically reduce  $\theta$ -phase growth.
- We determine that fine particles of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, trapped in the sample surface during the final step in the sample polishing procedure, will act as nucleation sites.
- We present a simple model that provides an excellent quantitative description of the oxide evolution.

## Model: Oxidation of β-NiAl at 1100 C

6-АЦО3 6-> Q

 $\theta\text{-Al}_2O_3(\text{yellow})$  forms before  $\alpha\text{-Al}_2O_3$  and grows rapidly. The oxide grows at the top surface (Al outward diffusion).  $\alpha\text{-Al}_2O_3$  (blue) subsequently nucleates and grows at the buried Interface by  $\bar{\theta} \, \Box \, \alpha$  conversion.



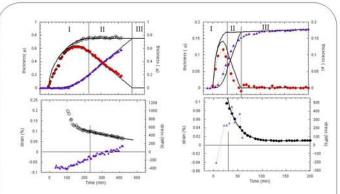
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 $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at buried interface cuts off outward flow of Al atoms. When metal/oxide interface becomes completely covered with  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, the growth of  $\theta$ -Al<sub>2</sub>O<sub>3</sub> stops and new oxide growth is  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> that results from  $\tilde{\theta} \square \alpha$  conversion.

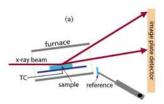


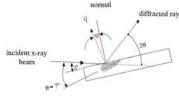
When  $\theta$  is totally consumed,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> scale grows much more slowly at metal/oxide interface (steady state growth).



Left panels: oxide thickness,  $\alpha$  and  $\theta$  phase strains for diamond polished sample.

Right panels: same for alumina polished sample. For the alumina polish, conversion is much more rapid leaving a thinner oxide when conversion is complete. Strains are initially tensile in  $\alpha\textsc{-Al2O3}$ , compressive in  $\theta\textsc{-Al2O3}$ . Solid lines are model calculations



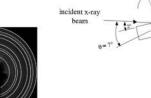


In-situ measurements at APS

with in-plane compressive stress
specimen surface d<sub>n</sub> 

with in-plane compressive stress

- (a) Schematic of the experimental setup.
- (b) Half rings of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reflections from oxidized NiAl sample. Strain is obtained from elliptical distortion of rings.
- (c) Full  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> Debye-Scherrer rings from the alumina reference.



With in-plane stress, Debye-Scherrer diffraction rings are elliptically distorted.

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